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Quality Considerations of Chloramine Disinfection

Thornton Utilities Dept., CO

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16. ABSTRACT
In attempting to solve their particular water quality problem, the City of Thornton, Colorado, observed some unusual results that may be applicable to other water systems in the country: the method by which chloramines are formed can significantly affect the ultimate water quality; when selecting alternative disinfectants, disinfection byproducts other than those currently regulated under the Safe Drinking Water Act should be considered; although one type of contaminant may be avoided through process modification, other, potentially less desirable contaminants may be produced.

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1986

QUALITY CONSIDERATIONS OF CHLORAMINE DISINFECTION

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INTRODUCTION

Like many communities throughout the United States, the City of Thornton, Colorado, is experiencing increasing contamination of their raw water supplies. This situation, coupled with the evermore restrictive finished water quality regulations, has caused the City to initiate a comprehensive water quality monitoring and treatment process testing program. The program, transcends the conventional applied research typically conducted at water utilities, and combines resources from private engineering, the public sector, and universities to manage and utilize results of both basic and applied research as a basis for problem solving. The water quality laboratory for the City of Thornton has played a vital role in the development and implementation of this particular program.

The City of Thornton receives its raw water from several separate sources surrounding the Denver Metropolitan area. As shown on Figure 1, Thornton is located just to the north of Denver along the South Platte River. One of its primary sources of water derives from shallow lakes adjacent to the South Platte River. The quality of this water is influenced by the urbanized area upstream. Both point discharges from wastewater treatment plants as well as urban runoff adversely affect the quality of water. Another source of water is Standley Lake, a reservoir within the Clear Creek Drainage Basin. Presently this watershed is less developed than the Platte, however, development pressures and new wastewater discharges are rapidly decreasing the quality of water in that particular basin.

Prior to 1978, the City of Thornton had very little water quality analytical capabilities within their laboratory and virtually no historical data on either the raw or finished water for their system. The required analyses for

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conformance with public health regulations were performed by outside laboratories or the Colorado Department of Health. At that time, the Thornton Utility Board recognized the need to develop in-house water quality expertise in order to begin to more effectively manage their system. At approximately this same time, high concentrations of nitrite (NO_2) were discovered within the distribution system, at times exceeding 2 mg/l. Based on data collected by the Thornton laboratory, the source of NO_2 was determined to be high concentrations of ammonia in the raw water. Due to the critical nature of the nitrite contamination, emergency treatment modifications were made. Breakpoint chlorination was instituted in an existing basin at the head of the water treatment plant to remove ammonia. Shortly after beginning breakpoint chlorination, the nitrite concentrations were reduced to near zero.

Once the immediate water quality problem was solved, evaluation of the breakpoint chlorination process continued. Although no specific data were available, there was speculation that due to the relatively high total organic carbon (TOC) concentrations in the raw water, high levels of chlorinated organics could be formed in the breakpoint chlorination process. Initial testing of the water following breakpoint chlorination confirmed that high concentrations of both total trihalomethanes (TTHM) and total organic halides (TOX) were being formed during the breakpoint chlorination process. At this time it was determined that further raw water monitoring would be necessary to characterize the quality of the raw water. Also, a pilot plant study was recommended to evaluate the effectiveness of existing treatment processes as well as additional processes for treating the available raw water supplies.

Pilot Plant Program

The Thornton Pilot Plant Program formally began in October, 1981 after several months of planning and design. The program was jointly funded by both the City of Thornton and the Environmental Protection Agency through a cooperative agreement.

The Thornton Pilot Plant Program consists of two major segments: a raw water monitoring program and a process testing program. The raw water monitoring program included sampling and testing of the various raw water supplies that are available to Thornton. The majority of the following parameters are analyzed once per month: Temperature, pH, DO, turbidity, alkalinity, calcium, hardness, TOC, I&T-THM, I&T T-TOX, TKN, NH_3,NO_3,NO_2, Total Coliform & Coliphage, and Metals. As the amount of data increases, water quality trends have been established which characterize the seasonal variations in raw water quality. These trends have been helpful in identifying and predicting raw water quality excursions such as episodes of taste and odor, elevated concentrations of metals and annual trends of trihalomethane formation potential.

The pilot plant process testing program involves operation of

a small conventional package water treatment plant followed by granular activated carbon columns. The conventional treatment processes are identical to those found in the full-scale water treatment plant. Figure 2 is a schematic diagram showing the process configuration and sample location points.

In the treatment process, potassium permanganate (0.4 to 0.6 mg/l) is added for iron and manganese removal and ferric chloride (5 to 20 mg/l) as the primary coagulant. Chlorine is also added for predisinfection. Following the addition of the chemicals, the water enters a premix basin having approximately 30 minutes detention time where it is vigorously mixed to promote the chemical reactions. Powdered activated carbon is added to the premix basin effluent at dosages of 2 to 4 mg/l for control of taste and odor.

Flocculation and sedimentation is accomplished in basins having a total detention time of approximately 135 minutes. Lime can be added to the clarifier for pH control at dosages up to 20 mg/l. Sludge is withdrawn from the bottom of the clarifiers for disposal.

The settled water is filtered using dual media filters loaded at approximately five gallons per minute per square foot. Chlorine is typically added to the filter effluent for post disinfection to achieve a total free residual of aproximately 2 mg/l.

The design flow rate for the pilot plant was established at approximately six gallons per minute, a condition which most closely matched the full scale facility detention time and resulted in similar process perfomance. Two pairs of granular activated carbon columns are used in the pilot facility: one pair follows both the sedimentation basin and the other follows the filters. The columns which follow sedimentation were used to evaluate the effectivenesss of replacing the filter media with granular activated carbon, and the columns following the filter evaluate the more conventional approach of post filtration adsorption. The pilot carbon columns consist of four, six-inch diameter, six-foot deep downflow glass columns which are operated in series. Each column has 5.5 feet of coal-base granular activated carbon (GAC) as media with six sample taps for monitoring organic breakthrough. The type of activated carbon was selected from bench scale laboratory tests to compare several alternative samples of commercially available carbon. The columns can be operated in series or in parallel with each having flow rates and retention times ranging from 1 gallon per minute per square foot to 4 gallons per minute per square foot.

The analytical program was designed to provide sufficient data to permit assessment of the treatment effectiveness of the various processes. Table 1 is a summary of the analytical program associated with the pilot process testing. The sampling was generally performed on a weekly basis with additional operational analyses as required for process control. In addition to the analyses summarized in Table 1, many short-term "side studies" were conducted to evaluate various anomalies observed in the data.

During the program, five separate treatment modes have been evaluated and a sixth is currently in progress. Each mode generally represents a refinement on the previous mode of operation relative to treatment effectiveness. Table 2 and Figure 2 summarize the various modes. Below are brief descriptions of each mode.

Mode 1

The Mode 1 configuration is identical to the full-scale treatment process configuration. Breakpoint chlorination is accomplished in the premix basin followed by coagulation, sedimentation and filtration. The primary purpose of conducting this mode was to assess the effectiveness of the pilot plant in approximating the performance of the full-scale plant. The results of Mode 1 indicated that the pilot plant actually matched the full-scale facility performance relatively closely.

Mode 2

Mode 2 differs from Mode 1 in that the breakpoint chlorination reaction is relocated downstream of the filter influent. The purpose of this modification was to maximize removal of organic precursors by flocculation and sedimentation prior to exposing the water to the high concentrations of chlorine required for breakpoint. It is interesting to note that the early results of this mode indicated that it was impractical to operate the facility without some level of disinfectant at the head of the plant to control biological slime growth. To prevent this from occurring, very small quantities of chlorine were added which combined with the natural ammonia present such that chloramines were formed. This mode of operation prevented the formation of the slime growth while allowing some precursor material to be removed. However, early results of this particular mode of operation did not show sufficient removal of precursor material to allow quality goals to be met.

Mode 3

This Mode is the same as Mode 2 with the exception that powdered activated carbon was eliminated from the process. The purpose of this particular mode was to evaluate the effectiveness of PAC in removal of organic precursors. The results of Mode 3 showed that powdered activated carbon in the doses normally applied at Thornton (2 to 4 mg/l) was not effective in organic precursor removal.

Mode 4

This Mode consisted of breakpoint chlorination in the premix basin followed immediately by the addition of ammonium sulfate to form chloramines. It was felt that breakpoint chlorination followed by rapid conversion to chloramines could reduce the time available for formation of trihalomethanes by the free chlorine. The results of

Mode 4 indicated that the time for initiation of reactions between chlorine and organic precursor material is very rapid at Thornton. Large increases from instantaneous to five day terminal trihalomethanes were observed during Mode 4. Figure 3 is a plot of the TTHM data for the pilot plant filter effluent.

Mode 5

As a result of Mode 4 configuration and the "competitive reactions" that appeared to be taking place between the chlorine and the organic material versus the chlorine and the ammonia, preparation of chloramine solution prior to introduction into the process stream was considered to be an alternative. The approach of forming a chloramine solution prior to addition to the process stream was used in Mode 5, and the results indicated that formation of trihalomethanes was virtually eliminated. However, this mode of operation resulted in much lower bactericidal effectiveness since no free chlorine was ever in contact with the raw water.

Mode 6

In an effort to avoid the undesirable bacteriological problems associated with Mode 5 while avoiding formation of chlorinated organics, a "dual disinfection" mode is currently being evaluated. This mode of operation consists of the use of both chloramines and chlorine dioxide fed to the raw water at the premix basin. Early results of the Mode 6 operation indicate that bactericidal effectiveness is enhanced greatly with the addition of chlorine dioxide. Total trihalomethane values are also apparently much less than when free chlorine is used as in Mode 4 and it appears that project goals can be met using this approach.

RESULTS AND DISCUSSION

As the Thornton Pilot Plant Program proceeded, several interesting observations were made which seemed to conflict with process performance experienced elsewhere. Although the findings discussed below may be unusual, it is felt that they should be considered when evaluating process modifications similar to those examined at Thornton.

During the early portion of the pilot plant program, it was discovered that terminal total trihalomethane (T-TTHM) concentrations appeared to increase at locations in the plant that followed breakpoint chlorination. After considerable investigation, it was determined that the amount of chlorine applied to a sample affected the resulting T-TTHM concentration even though sufficient free chlorine appeared to be present at the end of the holding period to meet established criteria for determining terminal trihalomethane. The extent to which the chlorine dose influence T-TTHM concentrations also appeared to vary throughout the year. Figure 4 is a plot of the slope of the chlorine dose dependency on T-TTHM formation for various waters available to Thornton.

The slope is defined as log $(T\text{-}THM_2/T\text{-}THM_1)$/log $((Cl_2)_2/(Cl_2)_1)$ where $TTHM_1$, $TTHM_2$ are the terminal trihalomethane concentrations and associated chlorine doses $(Cl_2)_1$ and $(Cl_2)_2$ respectively. Other studies conducted by EPA have reported values of the slope to be approximately 0.3. Figure 5 shows comparable chlorine dosage effects on T-TTHM formation for water from the Ohio River and Thornton's raw water along with associated chlorine residuals which are shown as vertical bars.

The chlorine dosage dependency is especially significant when evaluating data to assess organic precursor removal through treatment process. If significant dosage dependency exists, T-TTHM data may be difficult to interpret unless great care is taken in controlling the total amount of chlorine applied to a particular sample.

During Mode IV, a scheme which involved the addition of chlorine in concentrations sufficient to accomplish breakpoint followed immediately by addition of ammonium sulfate to form chloramines, several interesting observations were made. The first observation was that although no free chlorine was apparently present (as measured by the DPD method), significant amounts of T-THMs were formed. Measurements for residual chlorine and trihalomethanes are made both instantaneously and after the five day holding period. The data consistently showed the virtual absence of free chlorine after ammoniation. Instantaneous THM values are quite low (generally less than 20 ug/l). However, after the five day holding period at the ambient water temperature, the THM values were shown to at least double their values from the instantaneous values without the addition of more chlorine. The magnitude of the final THM concentration using Mode IV configuration at times approached 100 mg/l.

Several other tests were performed using other sources of raw water as shown in Figure 6. In addition, "Study No. 23" utilized commercially available ultra-pure water. The waters that did not contain natural ammonia were spiked with ammonia as shown on the figure. Breakpoint curves were developed for each water by adding chlorine to the samples and measuring chlorine residual. At each chlorine dosage point THM samples were collected. Results consistently show the formation of significant levels of trihalomethanes to the left of breakpoint.

Based on the results observed during the Mode IV operation, it is speculated that either competitive reactions are occurring between the chlorine and ammonia as opposed to the chlorine and organic precursors, or intermediate compounds are being formed which later result in formation of THMs.

During various periods throughout the Thornton Pilot Program, four separate conditions have been evaluated with respect to the standard breakpoint chlorination curve:

- Far to the left of breakpoint, primarily where monochloramines predominate.

- Just to the left of breakpoint, where dichloramines predominate.

- Following breakpoint chlorination with subsequent addition of ammonia.

- Formation during preparation of a chloramine solution prior to its addition to the main process water stream.

The chloramine concentrations under the above four conditions each are identical with respect to residuals as measured by the DPD method. However, the resulting water quality varied considerably with respect to trihalomethanes, total organics halides (TOX), organic chloramines (OCA), inorganic chloramines (ICA), dichloroacetonitrile, and bacteriological risk. Figure 7 is a relative comparison of the water disinfected with the four types of chloramines at Thornton. It should also be noted that the relative values vary somewhat between seasons of the year. Although most of the parameters are not regulated, they may be of concern relative to potential public health risk, and should be considered when selecting this type of disinfectant.

The performance of the granular activated carbon columns at Thornton generally showed a moderate reduction in trihalomethane formation potential. Figures 8 and 9 show typical GAC column performance with time. The T-THM-FP removal effectiveness is generally consistent with other findings with one significant exception. Results reported elsewhere suggest a "steady state condition" is reached after an initial period of operation where approximately 40 to 60% removal of the THM precursor material is realized. This condition is generally reached within approximately 20 weeks. Prior to this time, higher levels of removal are experienced. At Thornton, the steady state condition of 40 to 60% removal is reached almost immediately after the carbon is put in service with a gradual decline in the removal effectiveness thereafter. It is speculated that this condition results from relatively high loadings of organic precursors; or precursor compounds that are not readily adsorbed on activated carbon. Work is currently under way to better identify the size fractions of the organic compounds present.

Summary

In attempting to solve their particular water quality problem, the City of Thornton has observed some unusual results from their pilot plant program which could be applicable to other water systems around the country. The most notable observation is that the method by which chloramines are formed can have a significant impact upon the ultimate water quality. Utilities should consider disinfection by-products other than those that are currently regulated under the Safe Drinking Water Act when selecting alternative disinfectants. As seen at Thornton, although one type of contaminant may be avoided through process modification, other, potentially less desirable contaminants may be produced.

TABLE 1

PILOT PLANT CHEMICAL ADDITION POINTS
FOR RESPECTIVE MODES OF OPERATION

(SEE FIGURE 3)

MODE	$KMnO_4$	$FeCl_3$	Cl_2	P.A.C.	CaO	NH_4Cl	$(NH_4)_2SO_4$	ClO_2
1	A	A	A	B	C	-	-	-
2	A	A	D	B	C	-	-	-
3	A	A	D	-	C	-	-	-
4	A	A	A	B	C	-	B	-
5	A	A	-	B	C	A	-	-
6	A	A	-	B	C	A	-	A

FULL SCALE AND PILOT PLANT SAMPLING SCHEDULE

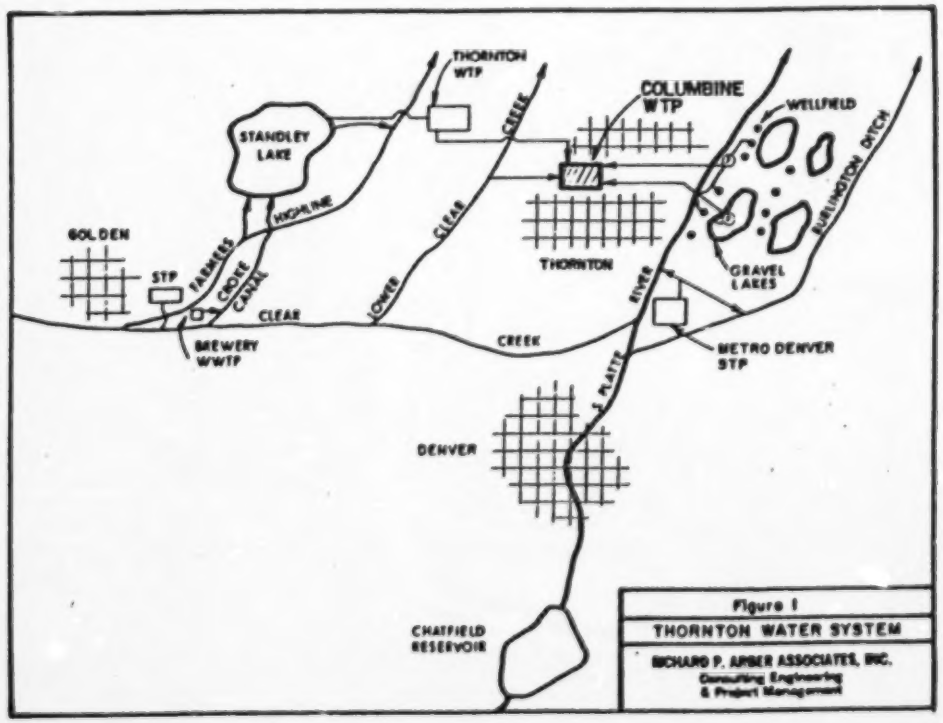
TABLE 2

Location	* I-THM	* T-THM (B)	* T-THM (ClD)	* I-TOX	* T-TOX (B)	TOC	Metals	SPC	Total Coliform	TKN	NH_3	NO_3	NO_2
1. FS RB	W&F	W&F	W&F	1/2wk	1/2wk	1/wk	1/qtr	1/day	1/day	1/2wk	W&F	1/wk	1/wk
2. FS PE	W&F	W&F											
3. PP PE	W&F	W&F											
4. FS CE	W&F	W&F									W&F	1/wk	1/wk
5. PP CE	W&F	W&F		1/2wk	1/2wk	1/wk		1/day	1/day		W&F	1/wk	1/wk
6. FS FE	W&F	W&F	W&F	1/2wk	1/2wk	1/wk	1/qtr	1/day	1/day	1/2wk	W&F	1/wk	1/wk
7. PP FE	W&F	W&F	W&F	1/2wk	1/2wk	1/wk	1/qtr	1/day	1/day	1/2wk	W&F	1/wk	1/wk
8. FS AD	W&F			1/2wk			1/qtr			1/mo	1/mo	1/mo	1/mo
9. CC 9-6	W&F	W&F	W&F			1/wk							
10. CC 10-6	W&F	W&F	W&F	1/2wk	1/2wk	1/wk	1/qtr	1/day	1/day				
11. CC 11-6	W&F	W&F	W&F			1/wk							
12. CC 12-6	W&F	W&F	W&F	1/2wk	1/2wk	1/wk	1/qtr	1/day	1/day				

FS - Full Scale
PP - Pilot Plant
RB - Raw Blend
PE - Premix Effluent
CE - Clarifier Effluent
FE - Filter Effluent
AD - Actual Distribution
CC 9-6 - Effluent of 1st GAC Column in series downstream of PP FE
CC 10-6 - Effluent of 2nd GAC Column in series downstream of PP FE
CC 11-6 - Effluent of 1st GAC Column in series downstream of PP CE
CC 12-6 - Effluent of 2nd GAC Column in series downstream of PP CE

W&F - Wednesday and Friday when the full scale plant is shut down and no special studies are scheduled. (otherwise, 1/wk)
1/wk - once per week
1/2wk - once per two weeks
1/qtr - once per quarter
1/day - once per day for three days each week
1/mo - once per month
* - pH, Temp. & Cl_2 analyses to be performed for all THM & TOX analyses
(B) - Chlorine residual 3 mg/l after 5 days
(C) - Chlorine residual 10 mg/l after 5 days
(D) - Chlorine residual 100 mg/l after 5 days

5/21/84 JG


THORNTON WTP
COLUMBINE WTP
WELLFIELD
STANDLEY LAKE
HIGHLINE
CLEAR CREEK
FARMERS
CROSS CANAL
GOLDEN
STP
LOWER CLEAR CREEK
THORNTON
GRAVEL LAKES
BURLINGTON DITCH
SOUTH PLATTE RIVER
BREWERY WWTP
METRO DENVER STP
DENVER
CHATFIELD RESERVOIR
Figure 1
THORNTON WATER SYSTEM
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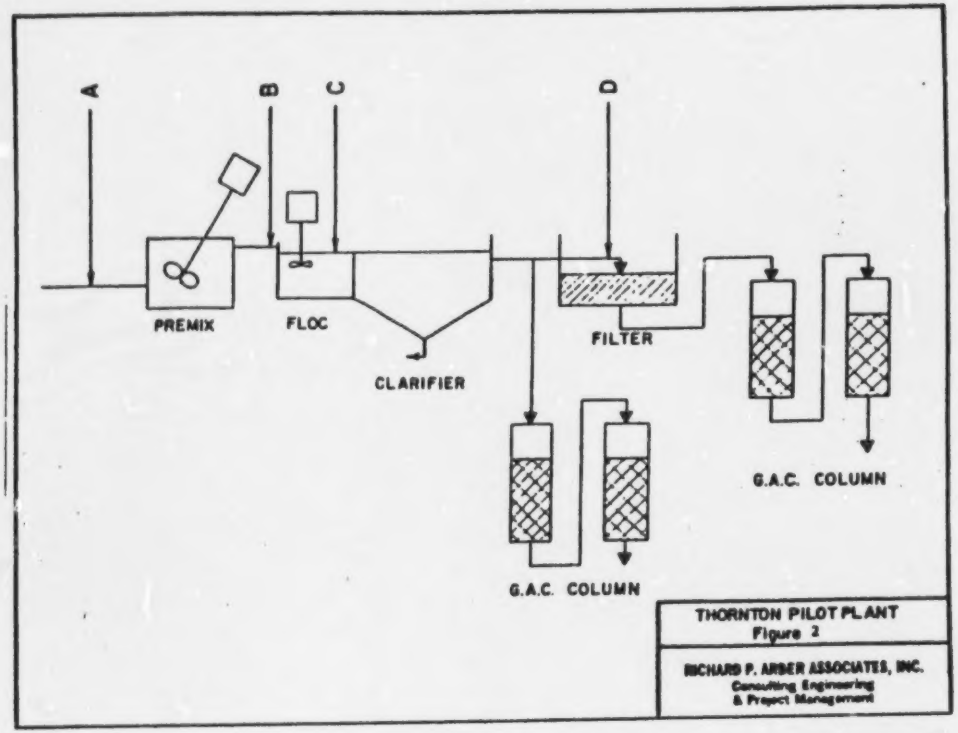
A
B
C
D
PREMIX
FLOC
CLARIFIER
FILTER
G.A.C. COLUMN
G.A.C. COLUMN
THORNTON PILOT PLANT
Figure 2
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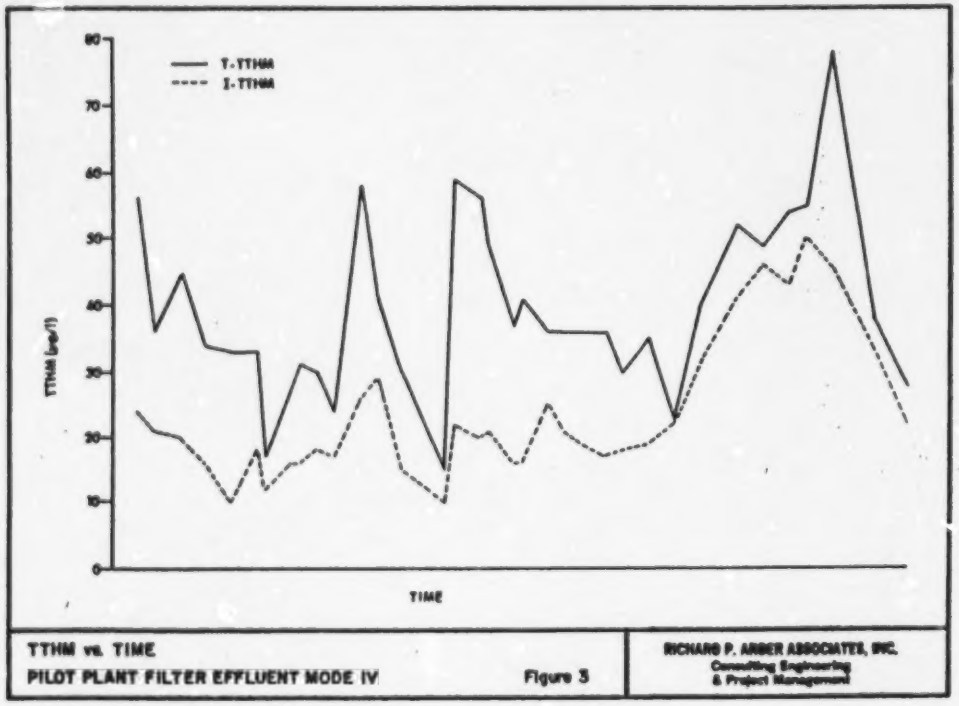

TTHM vs. TIME
PILOT PLANT FILTER EFFLUENT MODE IV

Figure 3

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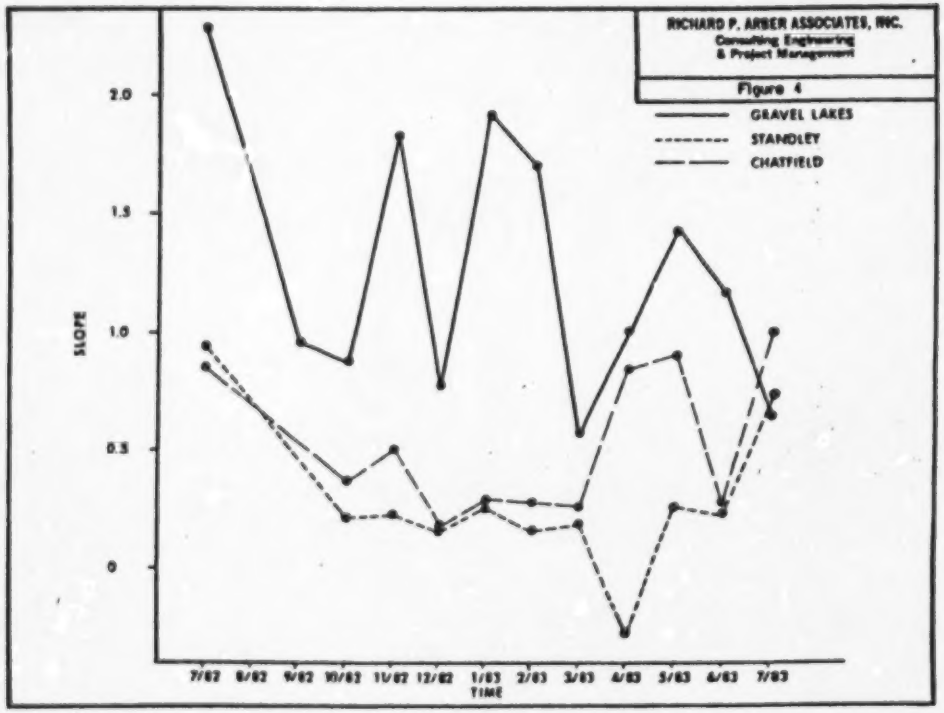
RICHARD P. ARBER ASSOCIATES, INC.
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Figure 4
GRAVEL LAKES
STANDLEY
CHATFIELD
SLOPE
2.0
1.5
1.0
0.5
0
7/82
8/82
9/82
10/82
11/82
12/82
1/83
2/83
3/83
4/83
5/83
6/83
7/83
TIME

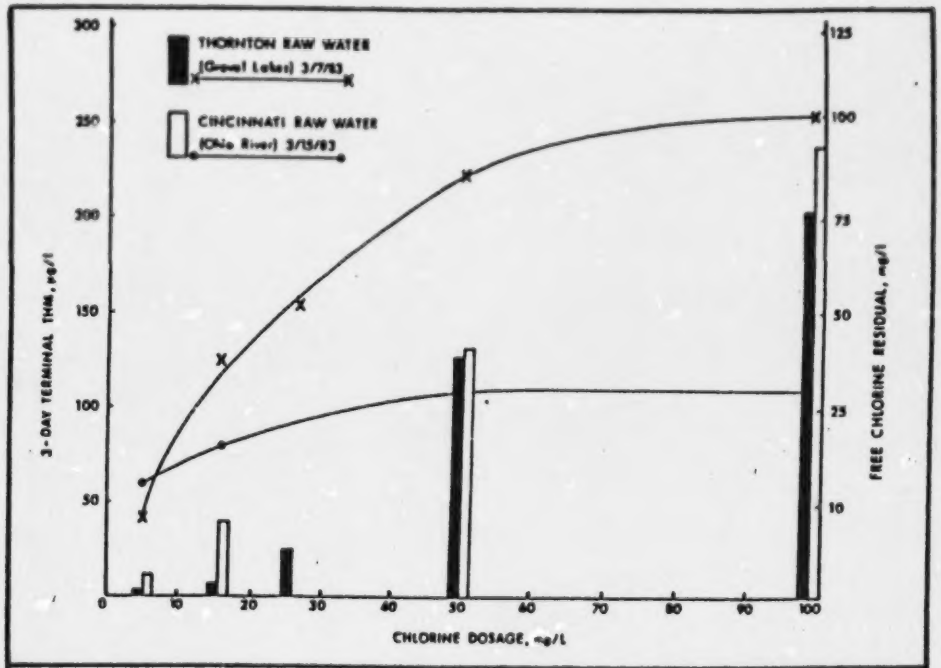

Figure 5
EFFECT OF CHLORINE DOSE ON THM CONCENTRATIONS FOR SURFACE WATERS

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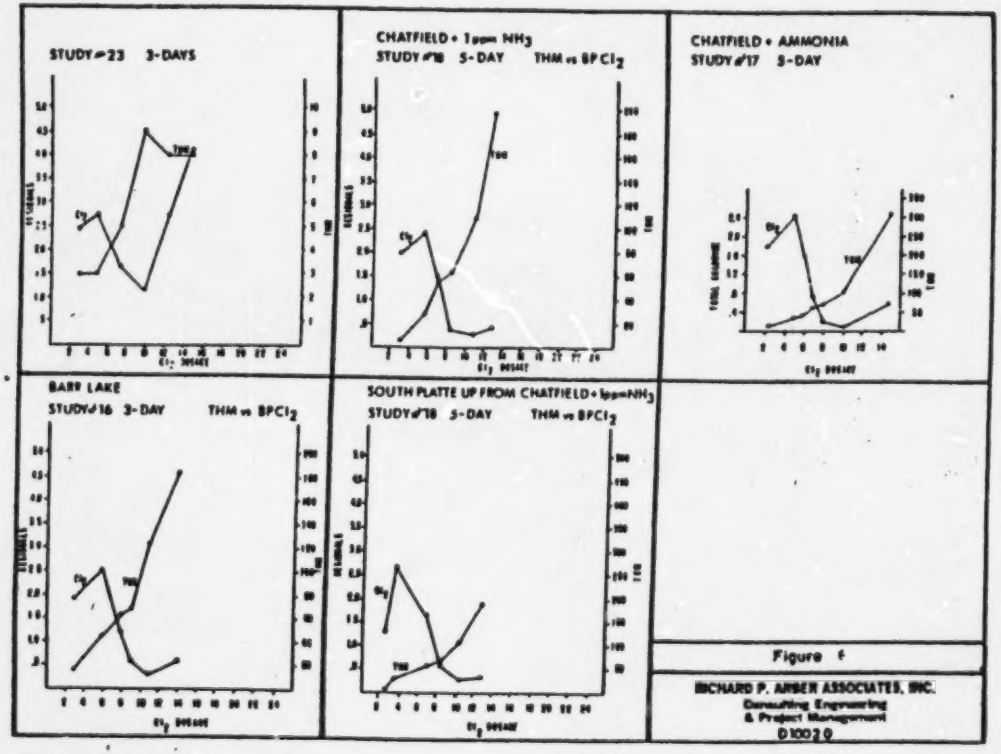
STUDY #23 3-DAYS
CHATFIELD + 1ppm NH3
STUDY #18 5-DAY THM vs BPCl2
CHATFIELD + AMMONIA
STUDY #17 5-DAY
BARR LAKE
STUDY #16 3-DAY THM vs BPCl2
SOUTH PLATTE UP FROM CHATFIELD + 1ppm NH3
STUDY #19 5-DAY THM vs BPCl2

Figure 1

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D10029

WATER QUALITY SPECTRUM AS A FUNCTION OF LOCATION ON THE BREAKPOINT CURVE
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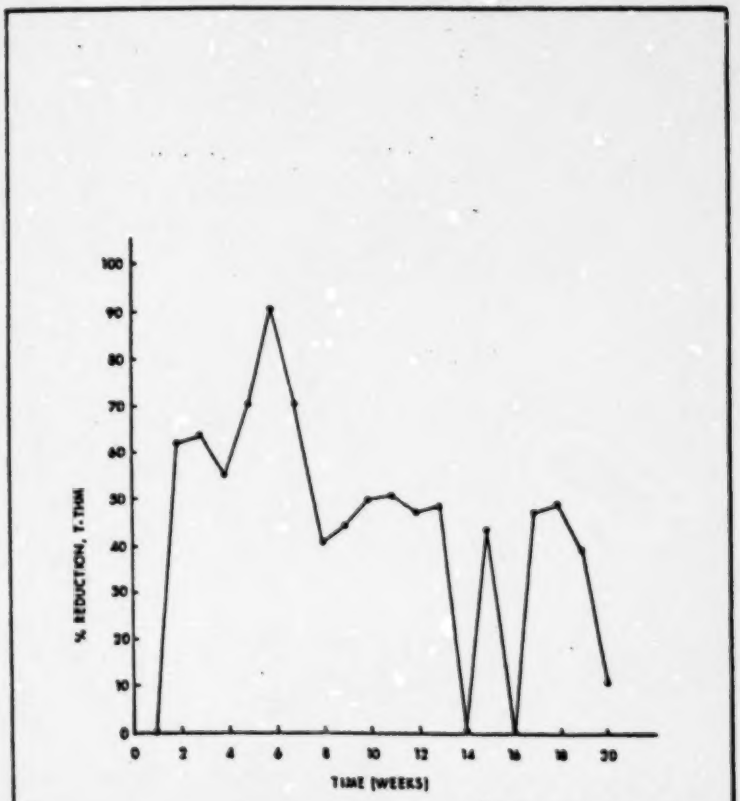
[1] [2] [3] [4] [5]
TTHM, DICHLOROACETONITRILE
OCA
BACTERIOLOGICAL RISK
TTOX
POINT 5 (WITH CHLORAMINE SOLUTION)
POINT 4
1
2
3

Figure 7



MODE I
G.A.C. PERFORMANCE

Figure 8

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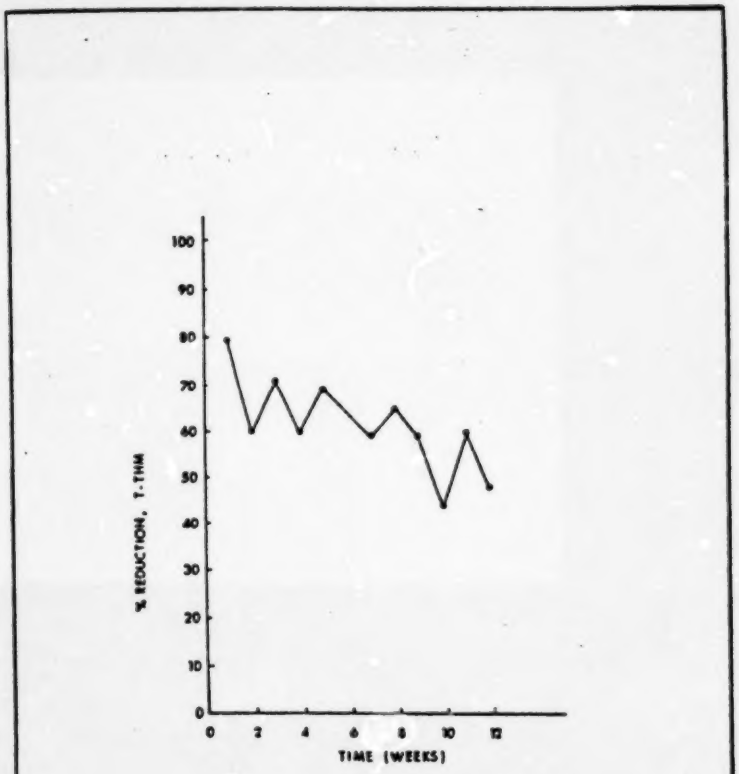

MODE V
G.A.C. PERFORMANCE

Figure 9

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